Indian Journal of Chemistry
Vol. 55A, February 2016, pp. 170-176

Notes

Tetraaquabis(4-methoxyphenylacetato-O') magnesium(II) dihydrate and catena-poly[[(diaqua)manganese(II)]-bis(μ_2-4-methoxyphenylacetato-O,O')]: A monomeric and a two-dimensional coordination polymer based on 4-methoxyphenylacetic acid

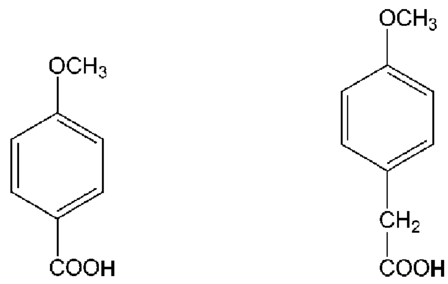
Kiran T Dhavskar & Bikshandarkoil R Srinivasan*
Department of Chemistry, Goa University, Goa 403 206, India
Email: srini@unigoa.ac.in

Received 2 November 2015; accepted 2 February 2016

The synthesis and characterization of tetraaquabis(4-methoxyphenylacetato-O')magnesium(II) dihydrate (**1**) and catena-poly[[(diaqua)manganese(II)]bis(μ_2-4-methoxyphenylacetato-O,O')] (**2**) based on 4-methoxyphenylacetic acid (4-mpaH) ligand is reported. In **1**, the unique 4-mpa functions as a monodentate ligand for Mg(II) situated on an inversion centre, resulting in a monomeric Mg(II) complex. The Mn(II) in **2** is also located on an inversion centre and the μ_2-bridging bidentate coordination mode of the unique 4-mpa ligand results in the formation of a two-dimensional manganese coordination polymer.

Keywords: Coordination polymer, Two-dimensional coordination polymers, Monodentate ligands, Bridging bidentate ligands, Methoxyphenylacetic acid, Manganese, Magnesium

As part of our long-standing research interest, we are investigating the structural chemistry of carboxylates of the *s*- and *d*-block metals. In earlier works we have reported the synthesis and characterization of several one-dimensional (1-D) coordination polymers especially of Ca using monocarboxylic acid linkers like 4-nitrobenzoic acid[1], 2-carbamoyl-4-nitrobenoic acid[2], 4-methoxyphenylacetic acid (4-mpaH)[3], etc. Use of dicarboxylic acids (ditopic), tricarboxylic acid (tritopic), and or bridging ligands can lead to two- or three-dimensional structures as shown recently by us for the Ca and Ba salts of the tritopic benzene 1,3,5-tricarboxylic acid[4]. In the pair of linkers 4-methoxybenzoic acid also known as *p*-anisic acid and 4-mpaH, the –COOH group (Fig. 1) is attached to a rigid six-membered ring in *p*-anisic acid, unlike in the aliphatic acid 4-mpaH where the –COOH group is more flexible and is attached to a $–CH_2$ unit. It is interesting to note that in the case of 4-mpaH and *p*-anisic acid, Ca(II) forms a 1-D and 2-D polymer[5] respectively. Apart from crystal structure of 1-D coordination polymers of Ca and Sm[6], study of La(III) complex of 4-mpaH for its antifungal properties is also reported[7]. A survey of the literature reveals that *p*-anisic acid in which the –COOH group is attached to a six-membered ring, can afford a 2-D structure for Mn(II)[8]. Hence it was of interest to see the coordination behaviour of the closely related and also the more flexible 4-methoxyphenylacetic acid ligand towards Mn(II). In addition we have also studied the corresponding Mg(II) salt of the same ligand. The flexible nature of the *s*-block metals to adopt to higher coordination numbers accompanied by the bridging binding mode of a carboxylate ligand normally results in the formation of compounds with an extended structure for metals like Ca, Sr and Ba. However, in the case of Mg(II), the carboxylate ligand often behaves as a mere charge balancing anionic species when syntheses are performed in aqueous medium under non-hydrothermal conditions. This is due to the tendency of Mg(II) to form the octahedral $[Mg(H_2O)_6]^{2+}$ species under such conditions. Therefore, it was of interest to study the behaviour of Mg(II) towards the more flexible 4-mpaH ligand under similar synthetic conditions. The results of these investigations describing the structure and characterization of tetraaquabis (4-methoxypheylacetato-O')magnesium(II) dihydrate (**1**) having formula $[Mg(H_2O)_4(4\text{-mpa})_2]\cdot 2H_2O$ and catena-poly[[(diaqua)manganese(II)]bis(μ_2-4-methoxy phenylacetato-O,O')] (**2**) of formula $[Mn(H_2O)_2(4\text{-mpa})_2]$ based on the 4-mpaH ligand is reported.


4-Methoxybenzoic acid
(*p*-anisic acid)

4-Methoxyphenylacetic acid
(4-mpaH)

Fig. 1—Rigid versus flexible –COOH group in *p*-anisic acid and 4-mpa**H**.

Experimental

All the chemicals used in this study were of reagent grade and were used as received from commercial sources without any further purification. Infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer from 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. UV-visible spectra were recorded in water using a Shimadzu UV-2450 double beam spectrophotometer with matched quartz cells. Isothermal weight loss studies were performed in a temperature controlled electric furnace. TG-DTA study was performed in flowing oxygen in Al_2O_3 crucibles at heating rate of 10 K min^{-1} using a STA-409 PC simultaneous thermal analyser from Netzsch. Magnetization measurements were carried out on a Quantum design Versa Lab vibrating sample magnetometer in an external field up to 3 Tesla in the range of 50 K to 300 K. ESR study was carried out on a Bruker EMx/micro-x instrument at room temperature.

For the preparation of $[Mg(H_2O)_4(4\text{-mpa})_2]\cdot 2H_2O$ (**1**), a mixture of 4-mpaH (1.329 g, 8 mmol) and magnesium carbonate (0.337 g, 4 mmol) in doubly distilled water (40 mL) was heated over a water bath for ~30 min till all the insoluble carbonate dissolved to give a clear solution. The hot reaction mixture was filtered and kept aside for crystallization at low temperature. The colourless crystals which separated out in a few days were collected by filtration. Yield: ~63%.

For the preparation of $[Mn(H_2O)_2(4\text{-mpa})_2]$ (**2**), a solution of sodium bicarbonate (0.672 g, 8 mmol) in doubly distilled water (30 mL) was added to 4-mpaH (1.329 g, 8mmol) to obtain the sodium salt of carboxylic acid. To this solution, $MnCl_2\cdot 4H_2O$ (0.792 g, 4 mmol) in doubly distilled water (15 mL) was added slowly. The resultant solution mixture was filtered and left aside for crystallization. Transparent, pale brownish crystals appeared within 2-4 days which were collected by filtration. Yield: ~ 78%.

Single crystal X-ray analyses of compounds **1** and **2** were carried out at the Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology Madras. X-ray data were collected on a Bruker AXS Kappa Apex II CCD diffractometer equipped with graphite monochromated Mo (Kα) (λ = 0.7107 Å) radiation. Intensity data for structure determination were collected through an optimized strategy which gave an average 4-fold redundancy. The program APEX2-SAINT (Bruker, 2004) was used for integrating the frames. Four-fold redundancy per reflection was utilized for achieving good multi-scan absorption correction using SADABS (Bruker, 2004). Besides absorption, Lorentz, polarization and decay corrections were applied to intensity during data reduction. The structures were solved by direct methods using SIR92[9] and refined by full-matrix least squares techniques using SHELXL-97[10]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms attached to the aromatic ring were introduced in calculated positions and included in the refinement by riding on their respective parent C atoms. The technical details of data acquisition and selected crystal refinement results are summarised in Table 1.

Results and discussion

Insoluble $MgCO_3$ was solubilised in a hot aqueous solution of 4-mpaH to obtain **1** in good yield. Crystals of **2** were obtained from a reaction of $MnCl_2\cdot 4H_2O$ with *in situ* generated sodium salt of 4-mpaH. The composition of both compounds was arrived at based on elemental analytical data and the amount of oxide residue obtained on pyrolysis. Both compounds which contain the bivalent metal:4-mpa in 1:2 ratio are differently hydrated; **1** contains six moles of water per mole of Mg while **2** has only two moles of water per mole of Mn. The presence of water in both **1** and **2** can be evidenced by the characteristic profile of the IR spectra in the 3500-3000 cm^{-1} region (Supplementary data, Fig. S1). A comparison of the spectra of **1** and **2** with that of the free acid further reveals that the band due to the –COOH group of the free acid occurring at 1703 cm^{-1} is shifted to lower energies in **1** and **2**, confirming the formation of carboxylate. The presence of the 4-methoxybenzoate chromophore can also be evidenced from the UV-visible spectra (Supplementary data, Fig. S2) of **1** or **2** in water which are very similar to that of the free ligand spectrum. The observed band at 286 nm for **1** (287 nm for **2)** can be attributed to the intraligand charge transfer of the aromatic acid. The DTA curves of **1** (Fig. 2) and **2** (Supplementary data, Fig. S3) exhibit a first endothermic event (96 °C for **1**; 108 °C for **2**) which can be assigned to the dehydration process based on the corresponding weight loss observed (23.35% for **1**; 8.55% for **2**) in the TG curve. This is

Table 1—Crystal data and structure refinement for $[Mg(H_2O)_4(4\text{-mpa})_2]\cdot 2H_2O$ (**1**) and $[Mn(H_2O)_2(4\text{-mpa})_2]$(**2**)

Emp. formula	$C_{18}H_{30}MgO_{12}$ (**1**)	$C_{18}H_{22}MnO_8$ (**2**)
Formula wt (g mol^{-1})	462.73	421.30
Temp. (K)	293(2) K	293(2) K
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions	a (Å) = 5.3462 (3); α (°) 85.249 (2)	a (Å) =17.5084 (7); α (°) = 90
	b (Å) = 8.2219 (4); β (°) = 81.336 (2)	b (Å) = 5.6246(3) β (°) = 104.711(3)
	c (Å) = 12.841 (1) γ (°) = 77.271 (2)	c (Å) = 9.2334(2); γ (°) = 90
Vol. (Å^3)	543.59 (5)	879.48(13)
Z	1	2
D_{calc} (mg/m^3)	1.414	1.591
Abs. coeff. (mm^{-1})	0.144	0.796
F(000)	246	438
Crystal size (mm^3)	0.35×0.30×0.30	0.35×0.30×0.25
θ range for data collect. (°)	2.54 to 26.00	2.41 to 26.00
Index ranges	$-6 \le h \le 6$	$-21 \le h \le 21$
	$-10 \le k \le 10$	$-6 \le k \le 6$
	$-15 \le l \le 15$	$-9 \le l \le 11$
Reflect. collected/unique	15475/ 2131 [R(int) = 0.0290]	11902/ 1716 [R(int) = 0.0409]
Completeness to θ	99.7 %	99.9 %
Abs. correct.	Semi-empirical from equivalents	
Max. and min. transmission	0.9582 and 0.9515	0.8258 and 0.7962
Refinement method	Full-matrix least-squares on F^2	
Data/ restraints/ parameters	2131/9/167	1716/3/133
Goodness-of-fit on F^2	1.065	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.1098	R1 = 0.0278, wR2 = 0.0641
R indices (all data)	R1 = 0.0476, wR2 = 0.1167	R1 = 0.0400, wR2 = 0.0714
Largest diff. peak and hole (e Å^{-3})	0.302 and -0.218	0.236 and -0.267

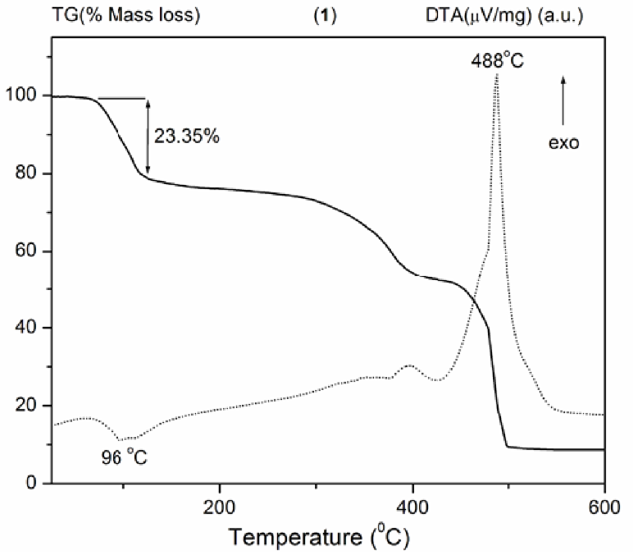


Fig. 2—TG-DTA curves of **1**. (For the TG-DTA curves of **2,** see Fig. S3).

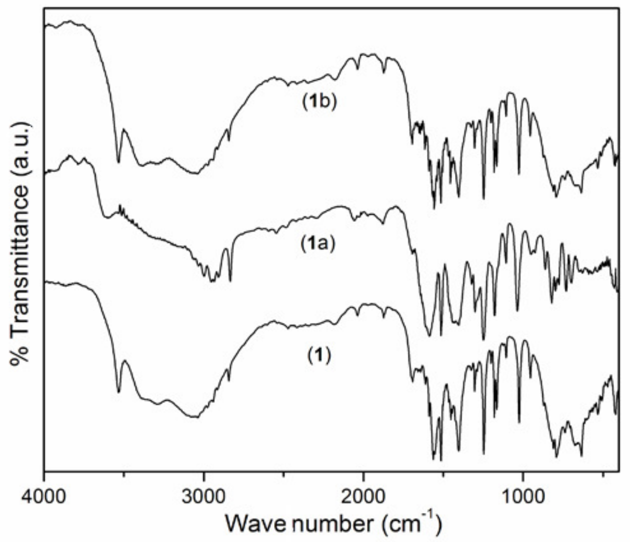


Fig. 3—Infrared spectra of compounds **1, 1a** (heated at 105 °C), **1b** (rehydrated) showing reversible hydration. (For the IR spectrum showing reversible hydration of **2**, see Fig. S4).

also verified by isothermal weight loss studies on heating **1** or **2** at 120 °C. Both the dehydrated complexes can be reversibly hydrated upon equilibration over water as evidenced by infrared spectra (Fig. 3 and Supplementary data, Fig. S4).

The ESR spectrum of **2** exhibits a broad isotropic signal centered at $g = 2.00$ (Supplementary data, Fig. S5). The broadness of the signal is due to spin exchange and dipolar interactions. The magnetic studies reveal paramagnetic behaviour of **2** at and below room temperature as shown in magnetization versus field and temperature plots of the compound (Fig. 4 and Supplementary data, Fig. S6). A magnetic moment of ~6.0 BM is observed indicating a high spin nature of Mn(II). Based on a combination of spectral data, weight loss study and elemental analytical data, compounds **1** and **2** are formulated as $[Mg(H_2O)_4(4\text{-mpa})_2]\cdot 2H_2O$ (4-mpa =

4-methoxyphenylacetate) and $[Mn(H_2O)_2(4\text{-mpa})_2]$ respectively.

Compound **1** crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with the central metal located on an inversion centre. The crystal structure consists of a central Mg(II) ion, two crystallographically independent terminal water ligands, a unique 4-methoxyphenylacetate anion and a lattice water molecule (Fig. 5). In view of the special position of Mg(II), the asymmetric unit consists of one half of the formula unit. In **1**, the 4-methoxybenzoato is coordinated to Mg(II) in a monodentate fashion and also functions as a charge balancing counter anion, with its geometric parameters in the normal range (Supplementary data, Table S1). Compound **1**, which contains Mg:H_2O in 1:6 ratio, is actually a tetraaquamagnesium(II) dihydrate and its crystal structure does not contain any $[Mg(H_2O)_6]^{2+}$ unit usually observed in several Mg(II) carboxylates. Instead its structure is made up of a $\{Mg(H_2O)_4\}$ square unit which is further linked to two *trans* monodentate 4-methoxyphenylacetate ligands resulting in a $\{MgO_6\}$ octahedron. The Mg-O bond distances range from 2.1122(11) to 2.2393(15) Å (Table 2). The *trans* O-Mg-O angles exhibit ideal values of 180° while the *cis* O-Mg-O angles vary between 87.37(5) and 92.63(5)°, indicating a slightly distorted $\{MgO_6\}$ octahedron.

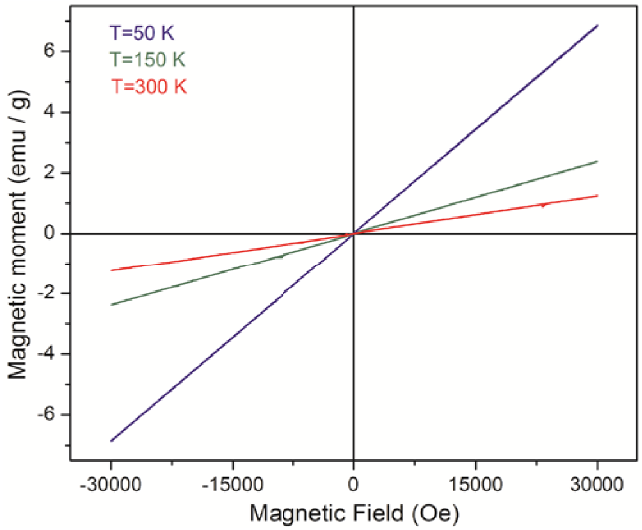


Fig. 4—Magnetization versus field (M-H) curve of compounds **2**. (For magnetization versus temperature (M-T) curve of **2**, see Fig. S6).

A few examples of tetraaqua Mg(II) compounds are known in the Cambridge Database and **1** closely resembles $[Mg(H_2O)_4(2\text{-nba})_2]$ (2-nba=2-nitrobenzoate), which contains two monodentate *trans* 2-nba anions linked to a tetraaqua Mg(II) unit, but no lattice water[11]. In **1**, the lattice water O6 serves to link four different neutral hexacoordinated $[Mg(H_2O)_4(4\text{-mpa})_2]$ molecules with the aid of O-H···O interactions (Supplementary data, Fig. S7). In addition to the H-atoms attached to the coordinated (O4 and O5) as well as the lattice water (O6), one H atom attached to C2 functions as H-donors while the carboxylate and the methoxy oxygens (O1, O2 and O3) of the monodentate 4-mpa and O6 of lattice water function as H-acceptors. It is interesting to note that unlike the Mg(II) salt of *p*-anisic acid which exhibits only O-H···O interactions in its crystal structure, both O-H···O and C-H···O interactions are observed in **1** (Table 3).

Compound **2** crystallises in the centrosymmetric monoclinic space group $P2_1/c$ with the Mn(II) situated in an inversion centre. Its crystal structure consists of a crystallographically unique Mn(II) ion, an independent 4-mpa anion and a unique monodentate

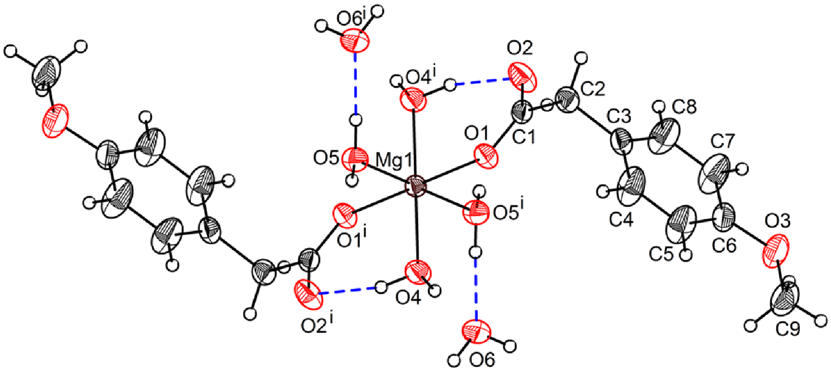


Fig. 5—Crystal structure of $[Mg(H_2O)_4(4\text{-mpa})_2]\cdot 2H_2O$ (**1**) showing atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level excepting for H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown by broken lines. [Symmetry code: i) -*x*, -*y*, -*z*+2].

Table 2—Selected bond lengths and angles of **1** and **2**

Bond lengths (Å)		Bond angles (°)			
$[Mg(H_2O)_4(4\text{-mpa})_2]\cdot 2H_2O$ (**1**)					
Mg1-O1	2.1122(11)	O4-Mg1-O1	91.84(5)	$O4^{i}$-Mg1-O4	179.999(1)
Mg1-O4	2.0493(12)	O4-Mg1-O5	89.72(5)	$O5^{i}$-Mg1-O1	92.63(5)
Mg1-O5	2.2393(15)	O5-Mg1-O1	87.37(5)	$O5^{i}$-Mg1-O5	180.00(7)
		$O4^{i}$-Mg1-O1	88.16(5)	O1-Mg1-$O1^{i}$	180.0
		$O4^{i}$-Mg1-O5	90.28(5)		
$[Mn(H_2O)_2(4\text{-mpa})_2]$ (**2**)					
Mn1-O1	2.1561(12)	O1-Mn1-$O1^{ii}$	180.0	$O1^{ii}$-Mn1-O4	90.76(5)
Mn1-$O2^{iii}$	2.1768(13)	O1-Mn1-$O2^{iii}$	89.67(5)	$O2^{iii}$-Mn1-O4	96.59(5)
Mn1-O4	2.2393(15)	O1- Mn1-$O2^{iv}$	90.33(5)	$O2^{iii}$-Mn1-$O4^{ii}$	83.41(5)
Mn-Mn ^{iv}	5.406	$O2^{iii}$-Mn1-$O2^{iv}$	180.0	O4 - Mn1- $O4^{ii}$	179.997(1)
		O1-Mn1-O4	89.24(5)		

Symmetry transformations used to generate equivalent atoms: i) -*x*,-*y*,-*z*+2 ii) -*x*+2, -*y*, -*z*+2; iii) *x*,-*y*-1/2, *z*-1/2 ; iv) -*x*+2, *y*+1/2, -*z*+5/2.

Table 3—Hydrogen bonding geometry for compounds **1** and **2**

D-H···A	*d*(D-H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	<DHA (°)	Symmetry code
$[Mg(H_2O)_4(4\text{-mpa})_2]\cdot 2H_2O$ (**1**)					
C2-H2B···O2	0.97	2.52	3.428(2)	155.0	*x*+1, *y*, *z*
O5-H5B···O6	0.895(16)	1.894(17)	2.7798(18)	170(2)	-*x*, -*y*, -*z*+2
O5-H5A···O1	0.897(15)	1.972(16)	2.8636(17)	172(2)	-*x*+1, -*y*, -*z*+2
O4-H4B···O2	0.894(16)	1.777(16)	2.6316(19)	159(2)	-*x*, -*y*, -*z*+2
O4-H4A···O6	0.889(16)	1.917(16)	2.8043(19)	176(2)	*x*+1, *y*, *z*
O6-H6A···O2	0.889(16)	1.821(17)	2.6979(18)	168(3)	*x*, *y*-1, *z*
O6-H6B···O3	0.878(16)	2.075(17)	2.891(2)	154(2)	-*x*, -*y*, -*z*+1
$[Mn(H_2O)_2(4\text{-mpa})_2]$ (**2**)					
C2-H2A···O4	0.97	2. 48	3. 349(3)	148.5	*x*, *y*, *z*
C9-H9B···O3	0.96	2. 63	3.461 (3)	145.6(3)	-*x*+1, -*y*, -*z*+3
O4-H4A···O1	0.852(17)	1.966(18)	2.779 (2)	159(3)	-*x*+2, *y*+1/2, -*z*+5/2
O4-H4B···O2	0.821(17)	2.50(2)	3.293(2)	162(3)	*x*, -*y*+1/2, *z*-1/2

D = Donor and A= Acceptor

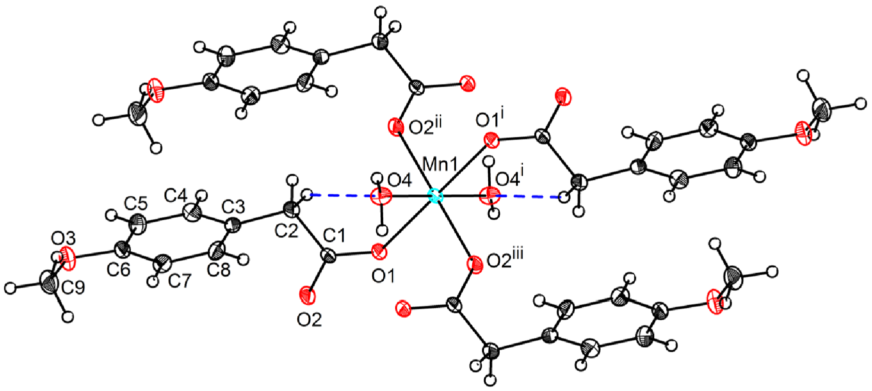


Fig. 6—The atom labelling scheme for $[Mn(H_2O)_2(4\text{-mpa})_2]$ (**2**) showing the hexa coordination around Mn(II). Displacement ellipsoids are drawn at the 50% probability level excepting for H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown by broken lines. [Symmetry code: i) -*x*+2, -*y*, -*z*+2; ii) *x*,-*y*-1/2, *z*-1/2 ; iii) -*x*+2, *y*+1/2, -*z*+5/2].

water molecule. The central metal is linked to four symmetry related 4-mpa ligands and two *trans* water molecules (Fig. 6). The hexa coordination can be explained due to the special position of Mn(II) and the presence of a unique μ_2-bridging bidentate 4-mpa ligand (O1, O2) and an independent terminal water (O4). It is interesting to note that the structure of **2** is quite similar to that of the corresponding *p*-anisate of Mn(II), namely [Mn(H_2O)$_2$(*p*-anisate)$_2$], which also exhibits hexa coordination around the central metal.

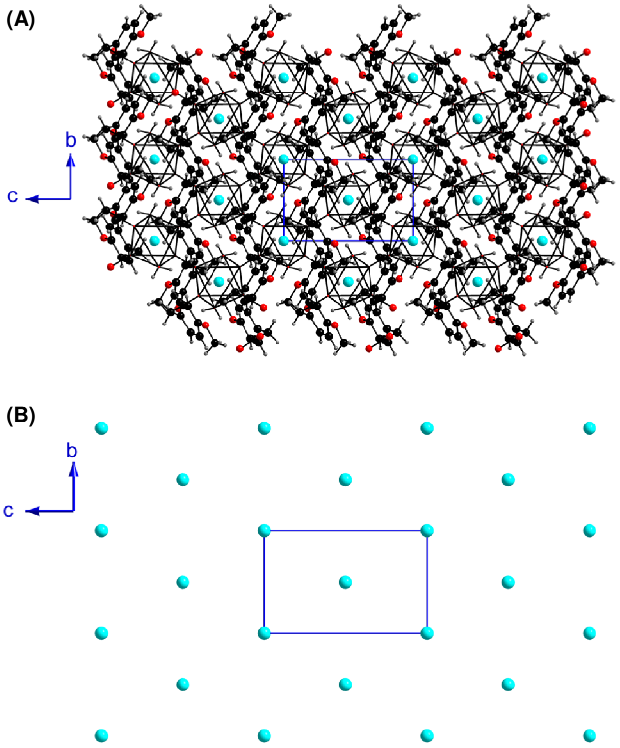


Fig. 7—(A) A view of the two-dimensional layer of Mn(II) ions in the crystallographic *bc* plane due to the μ_2-bridging bidentate binding mode of the unique 4-mpa ligand. The {MnO_6}units of **2** are shown as polyhedral. (B) For clarity the bridging lignads are removed to show only the Mn(II) ions in the layer which extend along the *b* and *c* axes with a Mn···Mn separation of 5.406 Å.

The geometric parameters of the unique 4-mpa ligand (Supplementary data, Table S2) are in the normal range and the μ_2-bridging bidentate ligand makes Mn-O distances of 2.1561(12) and 2.1768 Å (Table 2) respectively. The terminal water O4 is linked to Mn(II) at a longer bond distance of 2.2393(15) Å. The *trans* O-Mn-O angles exhibit ideal values of 180° while the *cis* O-Mn-O angles vary between 83.41(5) and 96.59(5)°, indicating a distorted {MnO_6} octahedron (Table 2). Two of the six vertices of the octahedron consist of the terminal (monodentate) water ligand (O4) disposed *trans* to each other and bonded to Mn(II). The remaining four vertices are occupied by the O atoms of the unique μ_2-bridging bidentate 4-mpa ligand (O1, O2), which links the Mn(II) ions into an extended chain with a Mn···Mn separation of 5.406 Å. This long distance between the adjacent Mn(II) ions is in accordance with the simple paramagnetic behaviour expected for high spin Mn(II) compounds. As each Mn(II) is bonded to four symmetry related 4-mpa ligands disposed *trans* to each other on four of the six vertices of the {MnO_6} octahedron, the Mn(II) ions extend along two directions, i.e., *b* and *c* (Supplementary data, Fig. S8) resulting in the organization of Mn(II) ions into a layer in the crystallographic *bc* plane (Fig. 7). As the Mn(II) ions extend along two axes due to the bridging nature of 4-mpa ligands, compound **2** is a two-dimensional coordination polymer.

Analysis of the structure reveals that the H-atoms of the coordinated water and the H atoms (H2A and H9B) attached to the methylene group and the methoxy group of 4-mpa function as H-donors and all the oxygen atoms, O1 to O4, function as H-acceptors resulting in two varieties of H-bonds, viz., O-H···O and C-H···O. Of these the C9-H2A···O4 interaction is an intramolecular H-bond while the C9-H9B···O3

Table 4—Comparative study of some compounds containing *p*-anisate and 4-mpa ligands

Compound	Space group	Binding mode	H-bonding	Dimension.	Ref.
[Mg(H_2O)$_4$(4-mpa)$_2$]^a	*P2$_1$/c*	Monodentate	O-H···O, C-H···O	Monomer	This work
[Mg(H_2O)$_6$]($C_8H_7O_3$)$_2$·2H_2O^{a}	*P2$_1$/c*	Charge balancing ion	O-H···O,	Monomer	4
[Ca(H_2O)$_2$(4-mpa)$_2$]^b	*P2$_1$*	Bidentate, μ_3-Bridging tetradentate	O-H···O C-H···O	1-D chain	2
[Ca(H_2O)($C_8H_7O_3$)$_2$]^b	*P2$_1$*	μ_2-Bridging bidentate μ_3-Bridging tetradentate	O-H···O C-H···O	2-D layer	4
[Mn(H_2O)$_2$(4-mpa)$_2$]^a	*P2$_1$/c*	μ_2-Bridging bidentate	O-H···O, C-H···O	2-D layer	This work
[Mn(H_2O)$_2$($C_8H_7O_3$)$_2$]^a	*P2$_1$/a*	μ_2- ridging bidentate	Not reported	2-D layer	8
[Sm(4-mpa)$_3$]·(H_2O)^b	*P-1*	Bidentate bridging Tridentate bridging	Not reported	1-D chain	6

interaction (symmetry code –*x*+1, -*y*, -*z*+3) is an intermolecular interaction involving an H-atom of the methoxy group in one chain with the methoxy oxygen in a perpendicular chain. It is interesting to note that a similar H-bond is also observed in the *p*-anisate salt of Ca(II), which exhibits a two-dimensional structure. However, no H-bonds involving the H-atoms of the methoxy substituent are observed in the Mg(II) and Ca(II) compounds of 4-mpa which is a one-dimensional polymer. We opine that the C-H···O bond involving the H-atoms of the 4-methoxy group is an important secondary interaction.

A comparative study of some structurally characterized metal compounds (Table 4) containing *p*-anisate or 4-mpa ligand reveals that the Mn(II) salts of both ligands are structurally similar and are two-dimensional polymers. In the case of Mg(II) both the compounds contain a $\{MgO_6\}$ octahedron and both are dihydrates. The Mg(II) salt of *p*-anisic acid is a hexaaquamagnesium(II) charge balanced by the anisate anion, unlike the 4-mpa anion which functions as a monodentate ligand in **1** in addition to charge balance.

In summary, the syntheses and structures of a monomeric Mg(II) compound of 4-mpa and a polymeric Mn(II) compound **2** of 4-mpa which exhibits a two-dimensional structure, are reported.

Supplementary data

Crystallographic data (excluding structure factors) for the structures of $[Mg(H_2O)_4(4\text{-mpa})_2]\cdot 2H_2O$ (**1**) and $[Mn(H_2O)2(4\text{-mpa})_2]$ (**2**) reported herein have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1433218 and CCDC 1433219 respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK. (fax: +44-(0)1223-336033 or email: deposit@ccdc.cam.ac.uk). Other supplementary data associated with this article, viz., Figs S1-S8 and Tables S1 and S2, are available in electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(02)170-176_SupplData.pdf.

Acknowledgement

The authors thank the Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology (IIT) Madras, Chennai, India, for single crystal X-ray analysis of **1** and **2** reported herein. Financial support under the Special Assistance Programme (DSA-1) of the University Grants Commission, New Delhi is gratefully acknowledged.

References

1 Srinivasan B R, Shetgaonkar S Y, Saxena M & Näther C, *Indian J Chem,* 51A (2012) 435.

2 Srinivasan B R & Shetgaonkar S Y, *J Coord Chem,* 63 (2010) 3403.

3 Srinivasan B R, Shetgaonkar S Y & Gosh N N, *J Coord Chem,* 64 (2011) 1113.

4 Srinivasan B R, Shetgaonkar S Y, Saxena M & Raghavaiah P, *Indian J Chem,* 51A (2012) 1064.

5 Dhavskar K T, Bhargao P H & Srinivasan B R, *J Chem Sci,* 2016 (http://dx.doi.org/10.1007/s12039-016-1037-9).

6 Aragón-Muriel A, Camprubí-Robles M, González-Rey E, Salinas-Castillo A, Rodríguez-Diéguez A, Gómez-Ruiz S & Polo-Cerón D, *Polyhedron,* 80 (2014) 117.

7 Aragón-Muriel A & Polo-Cerón D, *J Rare Earths*, 31 (2013) 1106.

8 Ghyragov F M, Musaev F N, Gambarov D G, Abbasov R M & Mamedov K S, *Koord Khim,*13 (1987) 1412.

9 *SIR92 - a program for automatic solution of crystal structures by direct methods*, *J Appl Cryst,* 27 (1994) 435

10 Sheldrick G M, *Acta Crystallogr* A64 (2008) 112.

11 Srinivasan B R, Shetgaonkar S Y & Näther C, *Z Anorg Allg Chem* 637 (2011) 130.